



Photocatalytic decomposition of NH_3 over TiO_2 catalysts doped with Fe

Kazutaka Obata, Kensuke Kishishita, Atsushi Okemoto, Keita Taniya, Yuichi Ichihashi*, Satoru Nishiyama

Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Hyogo, Japan

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ABSTRACT

The photodecomposition of NH_3 to H_2 and N_2 was carried out by using Pt-supported metal-doped TiO_2 (Pt/M- TiO_2 , M: dopant element) photocatalyst in an aqueous NH_3 solution under UV irradiation at room temperature. Fe-doped TiO_2 photocatalysts (Pt/Fe- TiO_2) promoted the highest yield of H_2 formation in the NH_3 photodecomposition. UV–visible diffuse reflectance spectra of Fe-doped TiO_2 showed that the absorption edge of TiO_2 was shifted from the ultraviolet to the visible light region by substitution with Fe. In addition, X-ray diffraction and electron spin resonance spectra showed that the dopant metals substituted a portion of the Ti^{4+} sites in the TiO_2 crystal without changing TiO_2 structure. Hence, it is indicated that TiO_2 doped with Fe can utilize visible light wavelengths and effectively produce hydrogen from the decomposition of aqueous NH_3 .

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1. Introduction

As global energy needs continue to increase, fossil fuel resources are depleted, and serious environmental problems arise; modern society has been seeking new technologies to effectively address these issues [1–4]. Hydrogen has been identified as a promising future energy carrier. There is much interest in finding ways to produce hydrogen from renewable energy supplies, such as solar and wind resources, to avoid the emission of greenhouse gases inevitably released by its production from fossil fuels. Photocatalytic water splitting using solar energy can contribute a solution to problems arising from environmental and energy issues related to hydrogen production [5–7]. However, water splitting cannot proceed without sacrificial carbon-containing materials such as methanol or ethanol.

The photodecomposition of ammonia is an anticipated methodology as hydrogen production processes implement these requirements [8–12]. The photocatalytic process proceeds at room temperature and atmospheric pressure by only using clean and inexhaustible light energy. Furthermore, ammonia has a number of advantages as a hydrogen storage carrier as follows: First, CO_2 is not exhausted in ammonia decomposition since it does not contain carbon. Second, ammonia can be easily transported and

stored, as severe conditions are not necessary for its liquefaction. Finally, hydrogen content percentage in one molecule (NH_3 : 17.6%) is high in comparison with that in other hydrogen storage carriers such as liquefied petroleum gas (LPG). As mentioned above, this photocatalytic process has the possibility of contributing to the establishment of a hydrogen energy recycling-based society.

Titanium dioxide (TiO_2) is an important semiconductor material used in a variety of applications, such as photo-splitting of water [1], photovoltaic devices [13], liquid solar cells [14], surface wettability conversion [15], and degradation of pollutants and toxic materials [16–19]. This wide applicability can be attributed to its nontoxicity, low cost, photostability, redox efficiency, and availability. However, the low efficiency of hydrogen production with TiO_2 is mainly due to its large bandgap (3.2 eV) located in the UV region of solar radiation, which accounts for only 4% of the incoming solar energy [20,21], rendering the overall process impractical. Therefore, any shift in optical response from the UV to the visible range will have a profound positive effect on the photocatalytic efficiencies of TiO_2 materials [22–24]. TiO_2 doped with other low-cost 3d transition metals such as Fe and Cr [5,25] can extend its light absorption to the visible spectrum and improve the separation efficiency of photo-induced electrons and holes. Owing to the two main reasons stated above, TiO_2 doped with these low-cost metals can also display a higher photocatalytic activity of H_2 production than undoped TiO_2 [5,25]. Furthermore, it should be noted that TiO_2 doped with Fe displays higher photocatalytic activity than TiO_2 containing other 3d transition-metal dopants [5,26–28]. Numerous studies

* Corresponding author. Tel.: +81 78 803 6433; fax: +81 78 803 6179.
E-mail address: ichiy@kobe-u.ac.jp (Y. Ichihashi).

pertaining to Fe-doped TiO₂ applied toward the decomposition of organic substances have been reported in the literature [29–36]. However, there are no reports of the application of TiO₂ doped with 3d transition metals toward H₂ production from ammonia. In this study, we have investigated the photodecomposition of ammonia by using several 3d transition metal-doped TiO₂ photocatalysts for the utilization of visible light.

2. Experimental

Metal-doped TiO₂ photocatalysts (M-TiO₂, M: dopant element) were prepared by a solid-state reaction [37]. A mixture of starting materials consisting of TiO₂ (Degussa P25), Cr₂O₃ (Nacalai Tesque), Fe₂O₃ (Nacalai Tesque), and H₂O was evaporated to dryness in a hot water bath at 363 K. The mixture was calcined at 1273 K for 10 h in air (M-TiO₂). For comparison, Fe loaded on a TiO₂ photocatalyst (Fe/TiO₂) was also prepared by the impregnation method with an aqueous solution of [Fe(NO₃)₃]·9H₂O. TiO₂ calcined at 1273 K was added into an aqueous solution in which the precursor was dissolved. The solution was evaporated to dryness in a hot water bath at 353 K. The sample was dried and then calcined under air-flow at 723 K (Fe/TiO₂). Platinization of M-TiO₂ or Fe/TiO₂ (Pt loading: 0.5 wt%) was carried out using a photodeposition method involving the irradiation of an aqueous suspension of TiO₂ with a 500 W Xe lamp for 2 h in the presence of methanol, H₂O, and H₂PtCl₆ [38]. After irradiation, the filtered Pt/M-TiO₂ sample was collected, washed with distilled water and then freeze-dried. The obtained sample was designated as Pt/M-TiO₂ (*n*) where *n* represents the content of metal doping.

The structural characterization of Pt/M-TiO₂ was carried out by X-ray diffraction (XRD) using Cu K α radiation (Rigaku RINT-2100). Diffuse reflection (DR) spectra were obtained using a UV–visible diffuse reflectance (UV–vis–DR) spectrometer (Hitachi U-3210D) and were converted from reflection to absorption by the Kubelka–Munk method. Electron spin resonance (ESR) signals from both Fe³⁺ and Ti⁴⁺ ions were recorded in the X-band ($\lambda \approx 3.2$ cm) at room temperature on a spectrometer using a quartz dewar. The ESR signals were registered by the lack of saturation in the field range of 500–5500 G.

The photocatalytic reaction was carried out in a quartz-glass batch reactor. The photocatalyst (40 mg) was suspended in 5 mL of ammonia aqueous solution (0.59 mol/L). The reactor was purged with an Ar gas flow for 15 min. The reaction solution was then stirred with a magnetic stirrer and irradiated with a Xe lamp (500 W) through a color filter (Hoya UV-25) for 8 h. The gas phase products were analyzed by gas chromatography (Shimadzu GC-8A) equipped with a thermal conductivity detector using Ar carrier gas.

3. Results and discussion

3.1. Photodecomposition reaction of aqueous ammonia

UV light irradiation of Pt loaded on TiO₂ photocatalysts (Pt/M-TiO₂) leads to the decomposition of an aqueous ammonia solution to hydrogen and nitrogen at room temperature. Table 1 shows the photocatalytic H₂ evolution from an aqueous solution of NH₃ over Pt-loaded TiO₂ photocatalysts modified with Fe or Cr (Pt/M-TiO₂, M = Fe, Cr) under UV light irradiation. In case of the reaction over Pt/TiO₂ with only H₂O as a reactant, no formation of H₂ was observed (Entries 1, 2). The photocatalytic activity of ammonia photodecomposition was increased when TiO₂ was doped with Fe (Pt/Fe-TiO₂), while the photocatalyst doped with Cr (Pt/Cr-TiO₂) showed almost similar photocatalytic activity as Pt/TiO₂ (Entries 2–4). Moreover, Pt/Fe-TiO₂ gave higher activity than TiO₂ impregnated with Fe (Pt/Fe-TiO₂, Entry 5). It is reported that when Cr³⁺ ions

Table 1

Photocatalytic yield of H₂ under various conditions: Pt loading, 0.5 wt%; Fe and Cr dopant, 1.0 wt%.

Entry no.	Catalyst	Reactant	Yield of H ₂ ($\mu\text{mol/g-cat.}$)
1	Pt/TiO ₂	H ₂ O	0
2	Pt/TiO ₂	NH ₃ + H ₂ O	18
3	Pt/Cr-TiO ₂	NH ₃ + H ₂ O	14
4	Pt/Fe-TiO ₂	H ₂ O	0
5	Pt/Fe-TiO ₂	NH ₃ + H ₂ O	27
6	Pt/Fe-TiO ₂	NH ₃ + H ₂ O	10

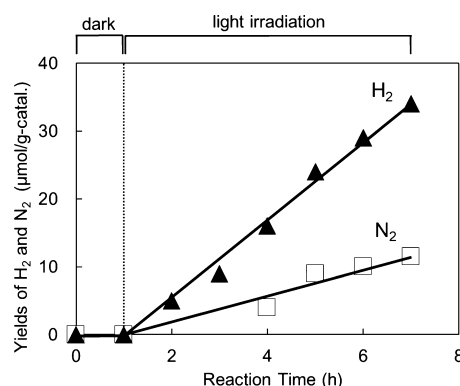


Fig. 1. Time profiles of H₂ and N₂ yields for the photodecomposition of NH₃ aq. over Pt/Fe-TiO₂.

are partly substituted for Ti⁴⁺ ions in TiO₂, oxygen defects and/or Cr⁶⁺ ions are formed to keep the charge balance [37,39]. Cr⁶⁺ ions may play a role in the recombination centers between photogenerated electrons and holes. It is thus suggested that, for the above reasons, the Pt/Cr-TiO₂ photocatalyst deactivated in comparison with Pt/Fe-TiO₂ photocatalyst.

Reaction activity was examined using the Pt/Fe-TiO₂ photocatalyst, which had the highest activity. Fig. 1 shows the time profiles of H₂ and N₂ yields in the photocatalytic reaction of NH₃ solution over Pt/Fe-TiO₂. The formation of hydrogen and nitrogen is observed as soon as the reaction solution is exposed to UV light irradiation. The formation of products is not observed under dark conditions. The above results indicate that this reaction proceeds photocatalytically. Small quantities of N₂ formation was detected at the reaction time of 2 h and 3 h, although it was hard to determine the quantity. Nitrogen and hydrogen was found to be produced by the ratio of 1:3 until 7 h (see Fig. 1). It was seemed that nitrogen and hydrogen stoichiometrically produced from NH₃. From the mass spectrometry by using the deuterium oxide (D₂O), the photodecomposition of NH₃ in D₂O solution caused not the formation of D₂, but the formation of H₂. Hence, hydrogen formation is established as being derived from the photodecomposition of ammonia. As shown in Fig. 1 and Table 1, Pt/Fe-TiO₂ also gave the highest yield of H₂ via NH₃ photodecomposition. Therefore, further investigation was carried out for the most active Pt/Fe-TiO₂ photocatalyst.

3.2. Characterization of Fe-TiO₂ photocatalyst

The UV–vis–DR spectra of several photocatalysts are shown in Fig. 2. As made evident from the spectra, the light absorption edge of Fe-doped TiO₂ (Fe-TiO₂) was remarkably red-shifted to the visible light range compared with both TiO₂ impregnated with Fe (Fe/TiO₂) and pure TiO₂. The red shift in the absorption edge of Fe-TiO₂ can be attributed to the excitation of 3d electrons of Fe³⁺ ions to the TiO₂ conduction band (charge-transfer transition) [25]. From the photoluminescence measurements of Pt/Fe-TiO₂, Pt/Fe/TiO₂, and Pt/TiO₂ catalysts, the photoluminescence spectrum attributed to the impurity band was observed in only Pt/Fe-TiO₂ catalyst. Therefore, it is

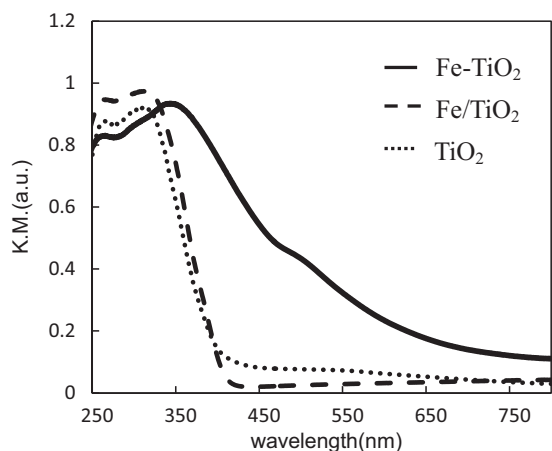


Fig. 2. UV-vis-DR spectra of Fe-TiO₂, Fe/TiO₂ and TiO₂ photocatalysts.

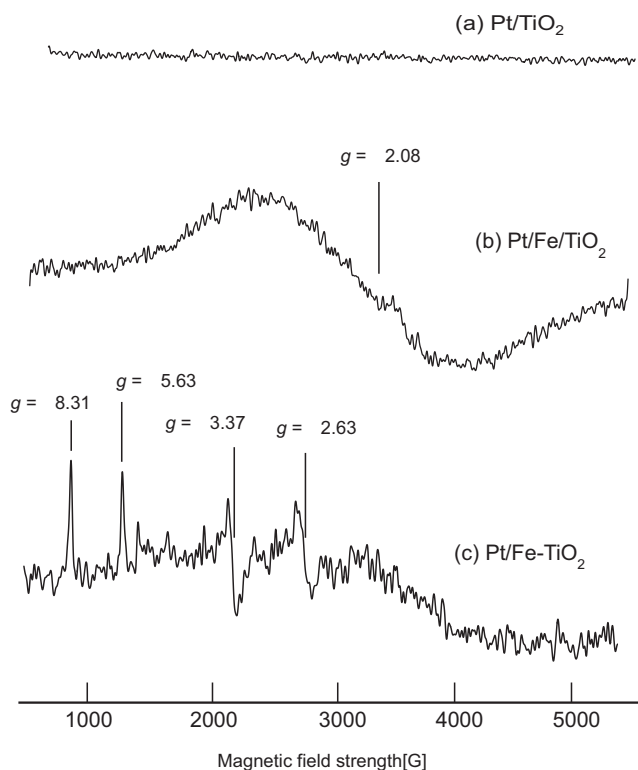


Fig. 3. ESR spectra of Pt/TiO₂ (a), Pt/Fe-TiO₂ (b) and Pt/Fe-TiO₂ (c) photocatalysts.

speculated that doping with Fe produces an impurity level in TiO₂. Accordingly, the substitution of Fe for Ti⁴⁺ may lead to the effective utilization of irradiated light. The decomposition of aqueous ammonia was also demonstrated over Fe loaded on TiO₂ photocatalysts prepared by an impregnation method (Fe/TiO₂). No effects attributed to Fe loading could be observed; the Fe/TiO₂ photocatalyst was not observed to utilize visible light ($\lambda > 420$ nm).

The ESR spectra of each catalyst are shown in Fig. 3. ESR spectroscopy is the technique for detecting and monitoring very low levels of transition metal-ion dopants [40]. Fig. 3(a)–(c) shows the spectra of Pt/TiO₂, Pt/Fe-TiO₂ and Pt/Fe-TiO₂, respectively. No peaks are observed in the spectrum of Pt/TiO₂ (see Fig. 3(a)); it is obvious that peaks attributed to Pt and Ti atoms are not observed. The spectrum of Pt/Fe-TiO₂ (Fig. 3(b)) has a signal at $g = 2.08$, which is assigned to the Fe³⁺ spin ($S = 5/2$) on the surface of TiO₂ [41,42].

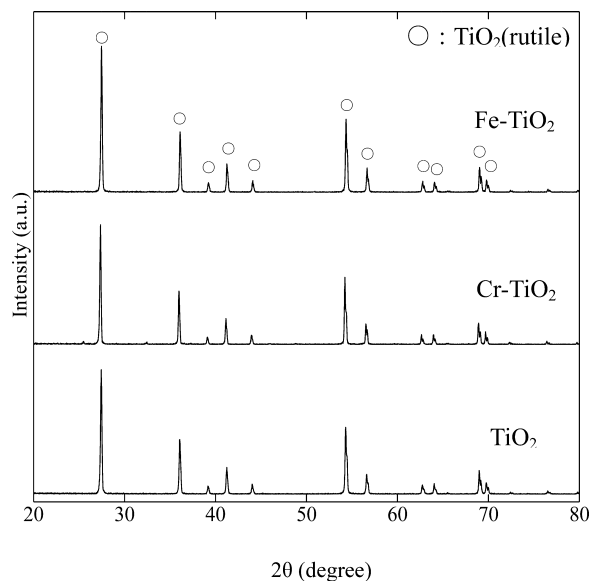


Fig. 4. XRD patterns of TiO₂ and metal ion-doped TiO₂ photocatalysts.

This observation verifies that Fe³⁺ exists within the anatase crystal lattice. In addition, the spectrum of the Pt/Fe-TiO₂ shown in Fig. 3(c) has signals present at $g = 2.63$, 3.37, 5.63, and 8.31, which are assigned to Fe³⁺ ions substituting for Ti⁴⁺ in the TiO₂ rutile lattice [43]. The Fe dopant can be inserted into the TiO₂ lattice as a Fe impurity band below the conduction band and above the valence band of TiO₂, creating an optical band gap [6,44]. It has been reported that electrons in the valence band of TiO₂ can firstly transfer to the Fe impurity band, and these electrons can then transfer from the impurity band to the conduction band through absorption of other photons. The excited electrons appear in the conduction band and holes in the valence band are subsequently formed [6]. Therefore, it is speculated that the substitution of Ti⁴⁺ with Fe³⁺ in Fe-TiO₂ leads to the effective utilization of irradiated light owing to the presence of a Fe impurity band.

Fig. 4 shows the XRD patterns of TiO₂ photocatalysts. Only rutile TiO₂ peaks were observed, and no peaks attributed to Fe or Cr species can be observed in these patterns. Fe³⁺ metal ions have an effective diameter comparable to those of Ti⁴⁺ ions. Thus, it is suggested that the dopant metals substituted for portions of the Ti⁴⁺ sites in TiO₂ crystal do not effect a change in the TiO₂ structure [37]. According to the above results obtained from UV-vis, ESR, and XRD analyses, it is speculated that TiO₂ has the ability to use not only UV light but also visible light by substituting Fe³⁺ for Ti⁴⁺ in its lattice.

4. Conclusion

Photocatalysts prepared by the loading of Pt on metal-doped TiO₂ (Pt/M-TiO₂) are shown to effectively decompose aqueous NH₃ to H₂ and N₂ under UV irradiation at room temperature. The Pt-loaded TiO₂ photocatalyst modified with iron (Pt/Fe-TiO₂) led to a higher activity than either chromium-doped (Pt/Cr-TiO₂) or undoped TiO₂ photocatalysts (Pt/TiO₂). It was found from UV-vis, ESR, and XRD measurements that by substituting Fe³⁺ for Ti⁴⁺, the resulting Fe-TiO₂ catalyst material might allow for the effective utilization of irradiation light owing to the presence of a Fe impurity band, thereby leading to its higher activity.

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